volts, and the differential ionization efficiency curves $\Delta I/\Delta V$ and $\Delta^2 I/\Delta V^2$ obtained by subtraction. This called for a high order of accuracy, not only in the measurement of I, but also in the equality of the intervals ΔV. Even with large analysed ion beam currents, the maximum accuracy which can be attained in the direct measurement of I is about 1 in 300. Accordingly, as the value of I increases, the scatter in the values of $\Delta I/\Delta V$ increases also, rapidly becoming as large as the values themselves. As ΔV requires to be as small as possible, it is difficult to obtain accurate differential *ie* curves over a range of more than a few volts above the initial onset of ionization.

If the mass spectrometer system is adjusted to detect a given ionic fragment, and the energy of the ionizing beam is set to some value V_1, a constant ion current I_1 is recorded which is proportional to the ionization efficiency for the process at that energy. If now a sinusoidal waveform of small amplitude and frequency f is superposed on V_1, a wave of the same frequency will be detected superposed on I_1. The peak-to-peak amplitude of the wave will be proportional to the first differential of the ionization efficiency at the energy V_1, and its phase with respect to the incident wave will be either 0° or 180°, depending on whether the sign of the differential is + or −. A detecting system which responds only to ac and is phase-sensitive will record this differential signal with an accuracy which is not dependent on the dc level of I_1. If V is now varied at a rate slow compared to f, the first differential *ie* curve will be traced out.[2] Further, if the ac detecting system is tuned to the second harmonic of the wave, i.e. $2f$, a voltage is obtained which is proportional to the second differential of the ionization efficiency at energy V_1, and by varying V the second differential curve can be traced out.[3]

This method of producing the second differential makes much less rigorous demands on the accuracy of the recording system, and the second differential ionization efficiencies can be recorded to as high an electron energy as desired. By its use the molecular electron spectra for a large number of molecules have been studied, and in all cases some details of structure are evident. The measurement of the lowest ionization potential of molecules is particularly simple, in that a sharp peak is obtained, the maximum of which gives a definite energy value.

In the figure are shown galvanometer traces of the first and second differential curves for the process $Hg \rightarrow Hg^+ + e$. The signal applied to the ionizing electron energy consists of a dc component, a periodic staircase waveform containing 60 steps which is repeated every 20 seconds, and a pure filtered sine wave. The gross details of the curve are recorded photographically using sine wave amplitudes of up to 1.0 volt peak-to-peak (ptp). This amplitude is then reduced to 0.1–0.2 volt ptp, the signal converted to digital form and correlated over a number of sweeps using the method described elsewhere,[4] in order to detect fine structure.[5] A fuller description of this technique and of the spectra obtained is being prepared for publication.

The author is indebted to Professor van der Pol for a discussion which contributed to the development of this method.

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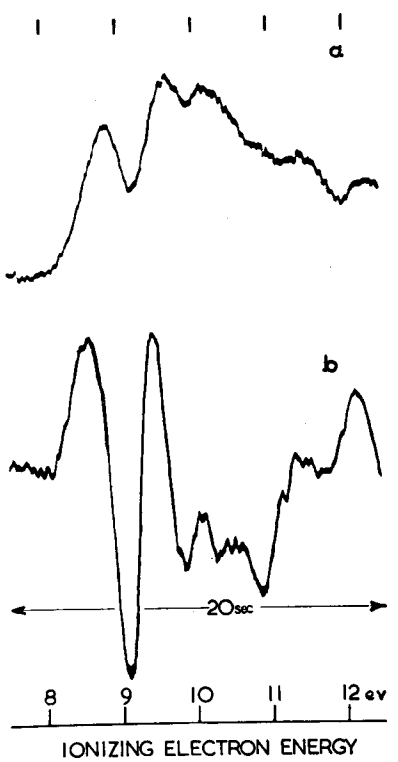

FIG. 1. First and second differential ionization efficiency curves for the process $Hg \rightarrow Hg^+ + e$ recorded directly with the mass spectrometer galvanometers over the range 7.5–12.5 ev. (a) First differential, sweep 5.0 volt, scanning sine wave, voltage 0.18 v, ptp 50 cps. (b) Second differential, sweep 5.0 volt, scanning sine wave, voltage 0.55 v, ptp 25 cps. Detecting system is tuned to 50 cps. Duration of sweep 20 seconds. The energy scale is not corrected for contact potential difference, etc.

The Photochemical Decomposition of Nitric Oxide by Absorption in the (0,0) and (1,0) γ Bands*

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THE abnormally large pressure broadening observed in the γ bands of NO[1,2] was interpreted by Wulf[3] as indicating a pressure-induced predissociation of the upper electronic state ($A^2\Sigma$). In an attempt to check this hypothesis Gaydon[4] irradiated NO at atmospheric pressure with the light from an iron arc and observed no evidence of decomposition after "long exposures."

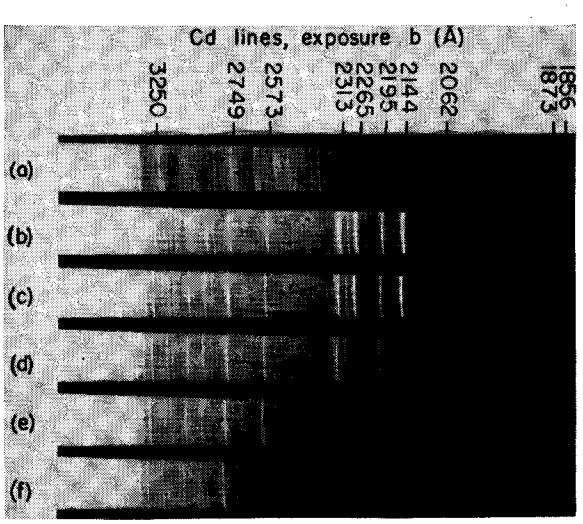

FIG. 1. All exposures were 100 seconds on a small Hilger spectrograph with the same slit width and source location. No lens was used between source and slit. (a) Iron arc, (b) Cadmium spark, (c) Cadmium spark filtered through 5.7 mm of NaCl, (d) Source as in (c) through a 25-cm absorption cell filled with NO to a pressure of 80 cm of Hg, (e) Through absorption cell after 15 minutes of irradiation, (f) Through absorption cell after 1 hour of irradiation.

Since the iron arc is a relatively weak source in the region of the γ bands (Fig. 1, exposure (a)), it was decided to repeat this experiment using a source with considerably more emission in this region.

A condensed spark between cadmium electrodes was chosen (exposure (b)) because of two strong lines at 2144 and 2265A, which overlap the (1,0) and (0,0) γ bands, respectively, (exposure (d)). In order to eliminate weak lines of higher frequency, the light was filtered through an NaCl plate, which was shown to eliminate effectively light of wavelength shorter than 2050A without appreciably weakening the desired lines (exposure (c))

Decomposition was followed by observing the continuous absorption of N_2O_3,[5] which is formed as an end reaction product Exposures (e) and (f) show the increase of this absorption after 15 minutes and 1 hour, respectively. That this decomposition was a photo effect by light in the region of the γ bands was demonstrated by experiments designed to rule out such possibilities as air leaks, induced electrical discharges, and light of higher frequency producing the decomposition products.

The observation of this decomposition is of interest because of its possible connection with the heat of dissociation of nitrogen. The absorbed lines have energies 5 77 and 5.46 electron-volts, considerably below the higher value for the heat of dissociation of nitric oxide (6.49 ev) as calculated from thermochemical data[6] and the two possibilities for the dissociation energy of nitrogen,[7] but more than the lower value (5.29 ev).

If the mechanism of this photo-decomposition of NO were shown to be predissociation, the lower value of the dissociation energy for NO and hence for N_2 would be established. Further experiments attempting to elucidate the mechanism will be undertaken.

* Contribution No. 1844 from the Gates and Crellin Laboratories, California Institute of Technology, Pasadena, California.
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PH_2D and PHD_2 Rotational Lines in the Region between 50 and 100 K

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THE rotational spectrum of phosphine and deuterophosphine have recently been investigated[1] by means of the far infrared spectrograph at The Ohio State University.[2] A study of the records made in attempting to obtain a spectrum of pure PD_3 shows that certain lines, not assignable to either PH_3 or PD_3, change their intensities from one record to another. The variation of intensity is so regular that certain of these lines may be associated with each of the partially deuterated phosphines, PH_2D and PHD_2.

Considerable difficulty was incurred in obtainlng a spectrogram of PD_3 and as a result a rather large number of records was made. If these records are arranged in order of the strength of the PD_3 lines one notices that some of the extra lines increase in intensity as the PD_3 concentration increases whereas others decrease in intensity. The data justify tentative identification of certain lines with PH_2D and certain others with PHD_2. Figure 1 shows a plot of the calculated PD_3 spectrum and an observed PH_3 spectrum along with two of the extreme records, a "poor sample" of PD_3 and therefore one strong in PH_3, and a "best sample" of PD_3 or one poor in PH_3. In these latter two spectra certain lines have been indicated by dots. The lines marked in the spectrogram labeled

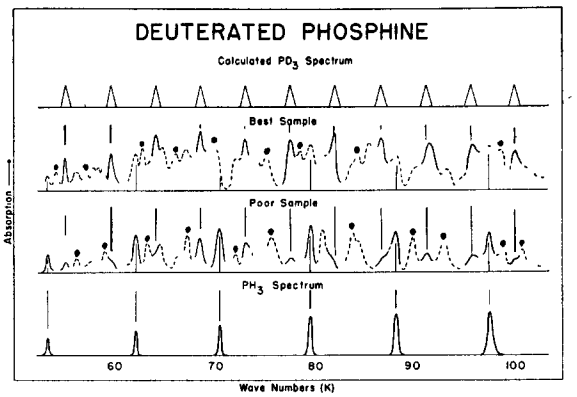

FIG. 1.

"best sample" have been assigned to PHD_2 and those lines dotted in the spectrograms labeled "poor sample" have been assigned to PH_2D. The values for the two sets of lines are listed in Table I.

TABLE I. Partially deuterated phosphine.

PH_2D	PHD_2
99.0 K	98.8 K
93.6	86.1
90.6	79.0
85.0	76.5
81.9	74.6
76.4	70.6
75.0	67.7
72.3	63.4
68.0	57.7
63 5	53.5
58.9	
56.1	

As the geometry of the phosphine molecule is known from the microwave investigations of Loomis and Strandberg,[3] it should be possible to predict the spectra of the partially deuterated phosphine and check the validity of the above assignments.

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Nuclear Magnetic Resonance Signals from a Tautomeric Mixture

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THE existence of keto-enol equilibria in β diketones and β keto esters was established by Kurt Meyer's bromine titration experiments.[1] The bromine titration technique has remained the most reliable method for determining the equilibrium ratio of the two forms. Studies of keto-enol equilibria have also been made by analysis of infrared[2] and ultraviolet[3] absorption spectra, and by refractive index measurements,[4] none of these methods has been generally applicable for providing accurate quantitative information on keto-enol equilibria.

We have succeeded in determining keto-enol equilibria in two β diketones by measurement of proton resonance with a high-resolution nuclear magnetic resonance spectrometer in the laboratory of Varian Associates at Palo Alto, California. Since this measurement cannot affect the equilibrium, it appears to be well